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**BENZOXAZOLE AND
BENZOTHIAZOLE ANTIRUST
GREASES**

Work Unit Directive (WUD) 51



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Benzoxazole and Benzothiazole Antirust Greases

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Perfluoroalkyl and perfluoroalkylether substituted benzoxazoles, benzothiazoles, bisbenzoxazoles, and bisbenzothiazoles have been synthesized and have been extensively tested as antirust and anti-corrosion additives in grease compositions based on fluorine-containing fluids and fluorinated ethylene-propylene (FEP) and polytetrafluoroethylene (PTFE) thickeners. Testing has shown that one percent concentrations of the additives in the grease formulations provide inhibition against rusting of ferrous metal components under conditions of high humidity. Testing in high-temperature environments has shown that corrosion of the ferrous metals is inhibited under these conditions also. Variations in fluid and thickener concentrations or grease consistency had no deleterious or synergistic effects on the inhibiting characteristics of the additives.

INTRODUCTION

With the advent of high-speed aircraft and aerospace vehicles and their support equipment, and the increase in their scope of operations under extreme conditions, severe demands have been placed on grease lubricants. Two of these demands are the provision of anticorrosion characteristics to grease-lubricated ferrous metal components operating at high temperatures while maintaining good antirust protection when these same grease-lubricated components are exposed to high-humidity conditions at mild temperatures.

While a grease in its simplest form consists of a lubricating fluid thickened by a solid to impart a semisolid consistency, the lubricant problems such as corrosion or rusting associated with specific applications have led to the evolution not only of advanced fluid and thickener materials, but also various types of advanced additives. New grease developments have selectively ensured improved antirust and anticorrosion characteristics. Among these are greases based on the various types of ethers and polysiloxanes; however, the thermal properties of these base materials are restricted

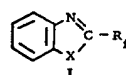
to temperatures in the range of about 200°C to 230°C. These shortcomings in the thermal properties of fluids have been overcome to a great degree by the evolution of the perfluoroalkylethers. It has been shown that greases can be produced from these fluorinated fluids by employing either fluorinated ethylene-propylene copolymer (FEP) or polytetrafluoroethylene (PTFE) thickeners. Greases formulated from these materials have proved to be able to provide good lubricating characteristics at temperatures as low as -40°C and -55°C and as high as 315°C. Although these greases have superior lubricating properties, and a wide temperature range, their utility is severely curtailed by their inability to prevent rusting of ferrous metal components in high-humidity environments. Their utility is also curtailed by their lack of anticorrosion properties when exposed to high temperatures (above 232°C).

Research has led to the development of fluorine containing additives which have overcome these rust and corrosion problems associated with perfluoroalkylether greases. Prominent among these fluorine containing additives are benzoxazoles and benzothiazoles.

SYNTHESIS OF ADDITIVES

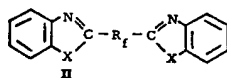
In the course of developing a lubricant capable of reducing the coefficient of friction and offering protection to metal surfaces against rusting and corrosion, a series of nitrogen heterocyclic compounds were examined as additives with rust- and corrosion-inhibiting properties. Since all the base fluids studied were highly fluorinated, the original premise of utilizing highly fluorinated additives to ensure compatibility with the fluids seemed justified.

Although there are numerous nitrogen containing heterocyclic compounds, the initial study was concerned with compounds indicated by the general structures:



where X = O or S

R_f = perfluoroalkyl,
perfluoroaryl or perfluoroalkylether



where X = O or S

R_f = perfluoroalkylene
or perfluoroalkylene ether

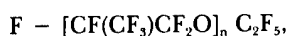
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DESCRIPTION OF PERFLUOROALKYLETHETHER FLUIDS

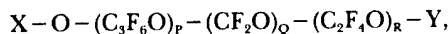
As a class of base fluids, the perfluoroalkylethers are characterized as having these properties:

- High degree of chemical inertness
- Excellent thermal stability
- Good lubricity
- Nonflammability
- High radiation resistance
- Good dielectric properties
- Excellent compatibility with plastics and elastomers
- Good nondeposit-forming properties
- Insolubility in most solvents
- Long-term reliability over wide temperature range

Two different perfluoroalkylether fluids were used in the development of the greases in this investigation. One of these fluids has the general formula



and the second fluid has the general formula



where X and Y are perfluoroalkyl. Both fluids are further distinguished by the properties given in Table 1.

TABLE 1—PROPERTIES OF PERFLUOROALKYLETHETHER FLUIDS

	FLUID 1	FLUID 2
Viscosity @ -18°C, cs	33 000	11 000
Viscosity @ 38°C, cs	270	90
Viscosity @ 100°C, cs	26	9
Viscosity Index	134	106
Pour Point, °C	-34	-34
Density, g/cc @ 25°C	1.9	1.9
Surface Tension, dynes/cm @ 26°C	19.6	20
Volatility, % wt loss 22 hours @ 204°C	4	10

DESCRIPTION OF THICKENERS

Two thickeners were used in these investigations. It was previously discovered that approximately equal thickening of the perfluoroalkylether fluids was exhibited by either an FEP copolymer or PTFE Ref. (1). Their properties are given in Table 2. The thickening characteristics of the FEP and PTFE are similar. Table 3 shows the results of FEP and PTFE grease formulations in which two types of perfluoroalkylether base fluids were used. The thickeners had no effect on the outcome of the tests for rusting and high-temperature corrosion. There was evidence of rusting or corrosion in only those tests in which no additive had been in the grease formulations.

RESULTS

Greases were formulated by mixing and stirring the fluid, thickener and additive components until a uniform mixture was obtained. The amounts of fluids used ranged from 65

TABLE 2—THICKENER PROPERTIES

	FEP	PTFE
Molecular weight range	120 000–190 000	2 000–50 000
Preferred MW range	140 000–160 000	10 000–50 000
Density, g/cc @ 25°C	2.4–2.5	2.2–2.3
Particle Size, micrometers	0.05–1.0	1.0–2.0
Surface Area, m ² /g.	10.1	7.6

to 72 percent by weight while the amount of thickeners ranged from 27 to 34 weight percent. Each grease composition contained one weight percent of the fluorine containing benzoxazole or benzothiazole additives. Greases were also formulated with no additive present to be used as controls for showing the additive effects. The grease mixtures were further blended to grease consistencies by passing them two times through a three-roll mill with the rollers set at an opening of 0.005 millimeter at about 25°C. The various grease compositions were tested according to standard test procedures.

Grease consistency was measured in accordance with ASTM D-217 method. The consistency of the greases have been expressed in NLGI grades. The NLGI (National Lubricating Grease Institute) has classified greases according to their worked penetration (the depth, in tenths of a millimeter, that a standard cone penetrates the grease sample under prescribed conditions of weight, time and temperature), and their classification ranges from 000 to 6 Ref. (2). The greases of this investigation were formulated to NLGI grades 1–2, or their penetrations ranged from 265 to 340 decimillimeters. The NLGI grades 1 and 2 are related below distinguished by the properties given in Table 1.

to the corresponding ASTM worked penetration range:

NLGI Grade	Worked Penetration Range
1	310–340
2	265–295

Rust preventive properties of the greases were determined in accordance with ASTM D-1743 method. This method provides for determining the corrosion protection properties of greases using grease-lubricated tapered roller bearings stored under wet conditions. Clean new bearings were lubricated as prescribed and were subsequently stored for 48 hours at 52°C and 100-percent relative humidity. At the end of the test, the bearings were cleaned and examined for evidence of corrosion. A bearing showing no corrosion is rated 1; insipient corrosion, no more than three small spots is rated 2; large spots or more than three small spots is rated 3. In this investigation the greases were rated passing (P) when there was no corrosion or only three small spots in evidence. When there were more than three small spots the grease was rated as failing (F).

There was massive corrosion exhibited in the control tests in which no additive was used to inhibit the greases against corrosion. Bearing specimens shown in Fig. 2 illustrate this absence of corrosion. When only one-half percent of the

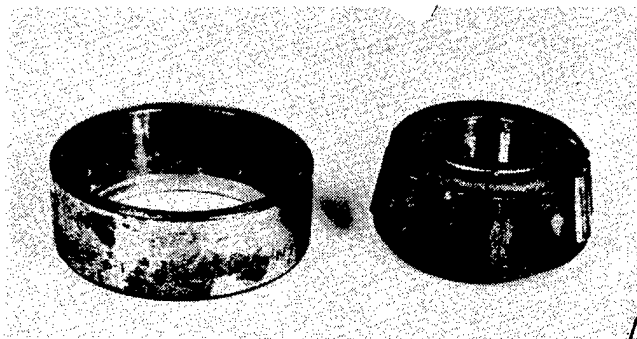


Fig. 1—Test bearing with extensive rusting

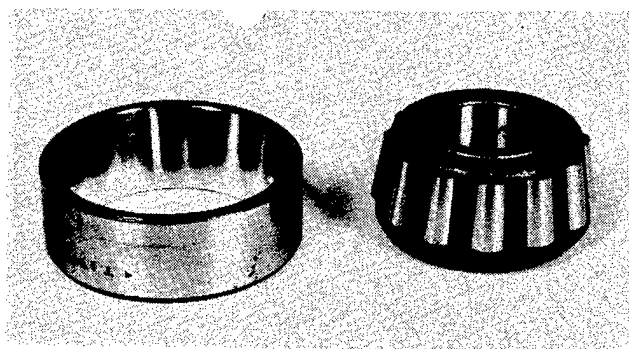
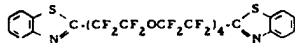
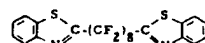
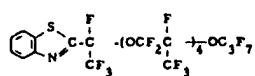
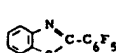
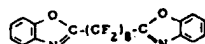
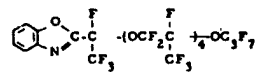
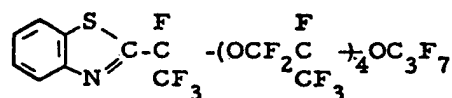


Fig. 2—Test bearing with no rusting

TABLE 3—GREASE FORMULATIONS AND RESULTS																	
BASE FLUIDS, %																	
F— $[(CF_3)(CF_2O)_n]_mC_2F_5$	70	70			65-72	65-72	65-72	65-72	65-72	65-72							
X— $O-(C_3F_7O)_p-(CF_2O)_q-(C_2F_5O)_r-Y$			70	70							65-72	65-72	65-72	65-72	65-72	65-72	65-72
THICKENERS, %																	
Fluorinated Ethylene-propylene (FEP)	30		30		27-34	27-34	27-34	27-34	27-34	27-34							
Polytetrafluoroethylene (PTFE)		30		30							27-34	27-34	27-34	27-34	27-34	27-34	27-34
ADDITIVES, %																	
					1						1						
						1						1					
							1						1				
								1						1			
									1						1		
										1							1
RESULTS																	
Grease Consistency, NLGI # (ASTM D-217)	2	2	2	2	1-2	1-2	1-2	1-2	1-2	1-2	1-2	1-2	1-2	1-2	1-2	1-2	1-2
Rust Preventive Properties (ASTM D-1743)*	F	F	F	F	P	P	F	P	P	P	P	P	P	P	P	P	P
High Temperature Corrosion, 232°C, 72 hours, (AFML-TR-69-290)*																	
52-100 Steel	F	F	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
440C Steel	F	F	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
M-10 Steel	F	F	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
M-50 Steel	F	F	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P

*P indicates Passing; F indicates Failing

additive was used, there was no apparent effect on the corrosivity of the greases, as there was still evidence of massive corrosion present. There was one exception to the above observations. The benzothiazole additive having the formula



did not provide prevention against rusting at any concentrations.

The corrosion characteristics of the grease were determined by a method which provides for half submerging steel balls in the grease sample for 72 hours at 232°C Ref. (3). A 0-4 rating system is provided for rating the severity of corrosion exhibited in the test:

- 0 - No stain or pitting
- 1 - Light to moderate stain
- 2 - Moderate corrosion
- 3 - Staining and pitting
- 4 - Massive corrosion and pitting

In this investigation, the greases were rated as passing (P) or failing (F). A rating of passing or failing was used because where there was a failure it was indicated by massive corrosion and pitting. In those tests where a rating of passing is indicated, there were no stains, no corrosion and no pitting. Examples of passing and failing specimens are shown in Figs. 3 and 4.



Fig. 3—Test specimen rated passing

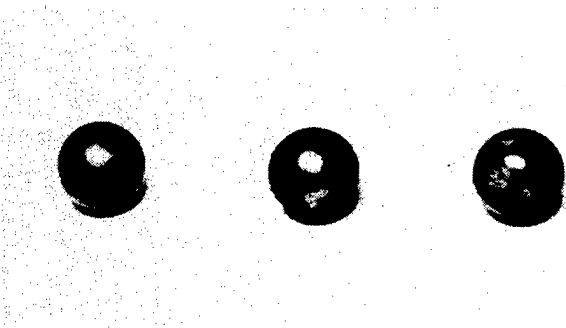


Fig. 4—Test specimen rated failing

Grease formulations containing no additive provided no protection for metals at high temperatures and corrosion was extensive as illustrated in Fig. 4. All of the greases containing at least one percent of the fluorine-containing additive exhibited good protection against corrosion of the metal specimens exposed to high temperature (above 232°C) for the prescribed time.

CONCLUSIONS

A variety of perfluoroalkyl and perfluoroalkylether substituted benzoxazoles, and bisbenzothiazoles have been synthesized through convenient synthesis procedures. Extensive testing of these compounds showed that they have antirust and anticorrosion additive properties when incorporated into greases based on fluorine-containing fluids. A one-percent-by-weight concentration of these additives was sufficient to inhibit against rusting and corrosion. Thickeners, e.g. fluorinated ethylene-propylene copolymers (FEP) and polytetrafluoroethylene polymers (PTFE) can be used in variable amounts with corresponding variation of perfluorinated fluids to produce greases with different consistencies. The concentration of additive is critical since less than one percent by weight offered no protection against rusting or corrosion to metal specimens under high-humidity mild-temperature conditions (~100°C) or conditions of high temperature (232°C or higher).

The technology developed by this study provides the guidelines for follow-on research and development on lubricants with higher temperature requirements (up to 316°C). Research efforts along these requirements are presently being formulated.

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- (1) Christian, J. B. and Arkles, B., "Polytetrafluoroethylene and Fluorinated Ethylene-Propylene Grease Lubricants," *Lubr. Eng.*, **30**, 3 (1974).
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- (3) Christian, J. B., "Rust Preventive and Corrosion Characteristics of Greases on Metals," AFML-TR-69-290 (January 1970).